Photoreactivity of Conjugated Bichromophoric Molecules; Photoreaction of *o*-Vinylbenzaldehyde with Secondary Amines

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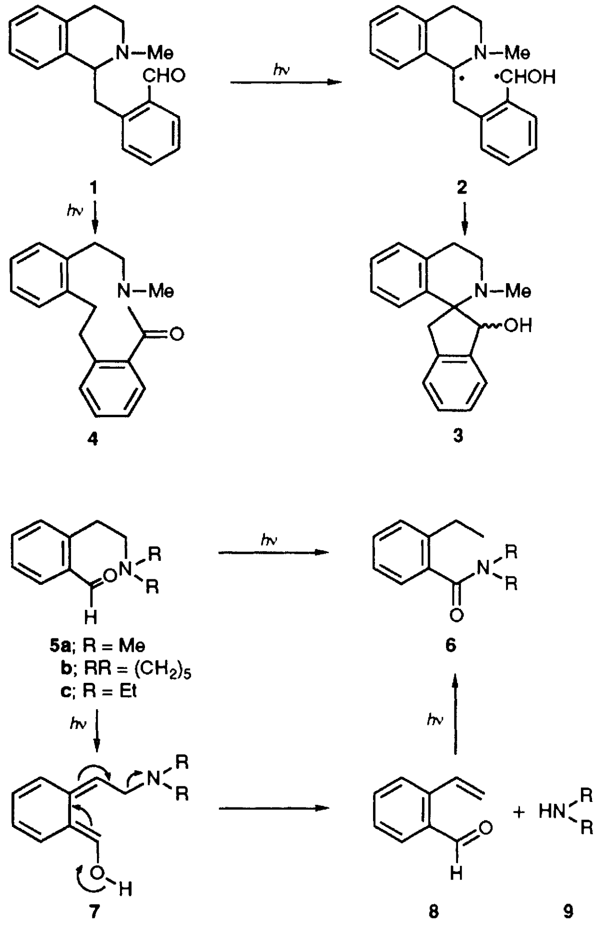
Irradiation of *o*-vinylbenzaldehyde **8** in the presence of secondary amines **9** results in N–H addition across the two chromophores to give *o*-ethylbenzamides **6**; photolysis of *o*-(2-dialkylaminoethyl)benzaldehdyes **5a** and **5b** also affords **6** *via* photoexpulsion followed by recombination of the **8** and **9** which are formed.

Photoreactions of carbonyl and styryl compounds with hydrogen donors have been studied extensively.[1] However, in spite of the attention commanded by photochemistry of bifunctional molecules in general,[2] substrates in which these two chromophores are conjugated do not seem to have been investigated. In this context, we report that irradiation of *o*-vinylbenzaldehyde with secondary amines affords *o*-ethylbenzamides in good yield. The reaction is unusual in that the carbonyl and the vinyl groups participate in conjunction, and addition of N–H occurs across these moieties.† The work has its origin in an attempted synthesis of spirobenzylisoquinoline alkaloids through photocyclisation of aldehyde **1**[4]‡ to alcohol **3**. Irradiation§ of an acetonitrile solution of **1** (1.7×10^{-3} mol dm^{-3}) for 2 h afforded **3** in moderate yield (20%), as a mixture of two isomers, along with a non-basic product (25%) which was identified as the amide **4**. Photolysis of the simple *o*-(2-dialkylaminoethyl)benzalde-



Scheme 1

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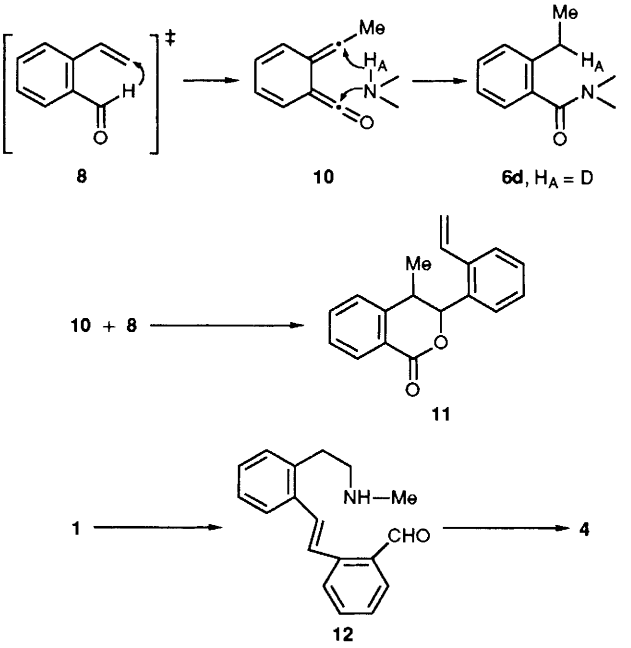
† Secondary amines are known to react with ketones, in the triplet excited state, by transfer of a hydrogen from an α-carbon to give radicals which undergo thermal reactions including pinacol formation. On the other hand in the case of styrenes reduction products are obtained *via* initial transfer of the amino hydrogen to a singlet excited state.[3]

‡ Satisfactory spectral data and elemental analysis by high resolution mass spectrometry were obtained for **1**, both isomers of **3**, and for **4**, **5a**, **5b**, **6a–d** and **11**. **6b**, ^{1}H NMR (90 MHz, CCl_4), δ −1.18 (t, 3H, Me), 1.60 (s, 6H, CH_2), 2.60 (q, 2H, CH_2), 2.86–3.33 (m, 2H, NCH_2), 3.70 (br s, 2H, NCH_2) and 6.96–7.40 (m, 4H, ArH); *m/z* 217, 216, 133 and 132; *m/z* 217.1461 (calc. 217.1467). **6d**, ^{1}H NMR (90 MHz, CCl_4) δ −1.20 (d, 3H, Me), 1.60 (s, 6H, CH_2), 2.58 (q, 1H, CH), 3.20 (br s, 2H, NCH_2), 3.69 (br s, 2H, NCH_2) and 6.94–7.44 (m, 4H, ArH); *m/z* 218, 217, 134 and 133; *m/z* 218.1529 (calc. 218.1529). **11**, ^{1}H NMR ($CDCl_3$, 60 MHz) δ −1.25 (d, 3H, Me), 3.3–3.6 (m, 1H, C*H*Me), 5.2–5.8 (m, 3H, C*H*$_2$=CH and C*H*O), 6.9–7.7 (m, 8H, ArH and ArC*H*=CH_2) and 8.0–8.2 (m, 1H, ArH); ν_{max} ($CHCl_3$) 1698 cm^{-1}; *m/z* 264, 249, 132 and 104; *m/z* 264.1140 (calc. 264.1150).



Scheme 2

hydes **5a** and **5b**[5] furnished the corresponding amides **6a** (55%) and **6b** (53%). Since extensive and unprecedented[6] bond reorganisation occurs in the transformation of **5** to **6**, involvement of consecutive photoreactions was suspected. Specifically, it was thought that *o*-vinylbenzaldehyde **8** and the secondary amine **9** formed *via* an initial photoexpulsion[7] may recombine in a different manner (**5** → **7** → **8** + **9** → **6**).[¶] Irradiation[§] of an acetonitrile solution of **8** (3.4×10^{-3} mol dm^{-3}) and piperidine (3.5×10^{-3} mol dm^{-3}) indeed furnished amide **6b** (85%). Similarly, amide **6c** was obtained (86%) from photoreaction of **8** and diethylamine.[¶]

The above reaction was quite inefficient if equimolar amounts of **8** and piperidine were used ($\phi_{disappearance} = 0.06$).[||] However, the quantum yield increased with amine concentration, although in an irregular fashion. The standard double reciprocal plot of quantum yield *vs.* amine concentration showed a downward curvature reminiscent of the pattern observed by Cohen *et al.*[8] in photoreactions of aromatic ketones with amines. This deviation from Stern–Volmer kinetics was attributed to ground state association and/or more than first order dependence on amine concentrations. Addition of 1 equiv. of piperidine to **8** (3.4×10^{-3} mol dm^{-3}) in acetonitrile resulted in no change in UV absorption (λ_{max} 308 nm, ε 2434). Fluorescence emission could not be detected from **8** or its mixture with piperidine. The reaction was not markedly sensitive to solvent polarity as it proceeded with comparable efficiency in benzene ($\phi = 0.08$). In the absence of nitrogen purging, the oxygen dissolved in the solvent did not exert any appreciable deleterious effect. Similarly, no quenching by *trans*-piperylene of cyclohexa-1,3-diene at a concentration equivalent to that of amine (3.4×10^{-3} mol dm^{-3}) was observed suggesting involvement of a singlet or a short lived triplet excited state.

A conceivable pathway to amide **6**, from **8** and **9**, is depicted in Scheme 2. The excited state of **8** may have charge-transfer character leading to a hydride shift from the carbonyl carbon to the electron-deficient vinyl terminus as suggested by a referee. Irradiation of an equimolar mixture of **8** and *N*-deuteriopiperidine gave the amide **6d**,[‡] as expected for nucleophilic attack by the nitrogen lone pair on the ketene carbon followed by D^+ transfer. Reaction initiated by transfer of amino hydrogen to the styryl side chain should lead to deuterium incorporation in the methyl group.[†] Efforts to trap **10** with added dienophiles like cyclohexene, methyl acrylate, acrylonitrile, dimethyl fumarate and maleic anhydride were unsuccessful, possibly as a consequence of the quick reversion and short lifetime of the *o*-quinodimethane intermediate. Amine trapping may be more effective because of prior complexation. However, from these experiments isocoumarin **11** formed by [2 + 4] cycloaddition of the carbonyl double bond of **8** across the diene **10**, could be isolated in low yield.[‡] No definite products could be identified from photoreaction of **8** with tertiary amines whereas primary amines afforded the corresponding amides. Lastly, the intriguing ring expansion of **1** to **4** can now be explained in terms of an intermediate **12** in which the carbonyl and the styryl functions are juxtaposed for conjunctive photoreaction with the amino group **1** → **12** → **4**.

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[§] Preparative photoreactions were carried out with nitrogen-purged solutions using a 450 W medium-pressure mercury lamp in a Pyrex immersion well.

[¶] No reaction between **8** and **9** was observed in the absence of irradiation. Addition of 1 equiv. of HCl completely inhibited the photoreaction. Irradiation of equivalent amounts of benzaldehyde, styrene and piperidine in acetonitrile gave 1,2-diphenylethane-1,2-diol and amide formation was not detected. Irradiation of acetonitrile solution of **8** containing excess of methanol or ethanol gave the corresponding *o*-ethylbenzoates in *ca.* 30% yield.

[||] All quantum yield measurements were carried out in matched quartz tubes in a merry-go-round apparatus using 313 nm light, filtered through a 2 mmol dm^{-3} solution of potassium chromate in 5% aqueous potassium carbonate (P. J. Wagner and D. A. Ersfeld, *J. Am. Chem. Soc.*, 1976, **98**, 4515). A concentration of 3.4 mmol dm^{-3} of **8** was used, and its disappearance, up to 15% conversion, was monitored by its UV absorption at 308 nm. A benzophenone–benzhydrol actinometer was used for light intensity measurement (W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, 1961, **83**, 2789). ϕ Values are based on average of at least three runs (ϕ, ±10%). A maximum ϕ value of 0.17 was obtained for an amine concentration of 0.1 mol dm^{-3}.

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